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O-(2,4-Dinitrophenyl) Oximes. Synthesis and Cyclization to 5,7-Dinitrobenzofurans

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We have recently reported (1) the application of the Fischer indole synthesis to the preparation of benzofurans. We wish to describe here the Fischer cyclization of *O*-(2,4-dinitrophenyl) oximes (III) to 5,7-dinitrobenzofurans (IV).

Some compounds of the type (III) were reported in the literature (2), prepared by condensation of oximes with 2,4-dinitrochlorobenzene. We synthesized these compounds directly from the carbonyl compounds, condensing them with *O*-(2,4-dinitrophenyl)hydroxylamine (II).

A previous attempt to synthesize compound II by Ilvespaa and Marxer (3) was reported to fail because of the sensitivity of the aminooxy group. We prepared II by condensing *t*-butyl *N*-hydroxycarbamate (4) with 2,4-dinitrochlorobenzene and treating the resulting *t*-butyl *N*-(2,4-dinitrophenoxy) carbamate (I) with trifluoroacetic acid.

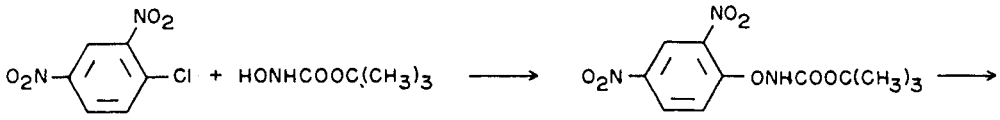
O-(2,4-Dinitrophenyl) hydroxylamine (II) condensed readily with aldehydes and ketones to give *O*-(2,4-dinitrophenyl) oximes (III). Over sixty compounds of this type were prepared but only those used for cyclization are described here.

2,4-Dinitrophenylhydrazones undergo the Fischer reaction only under severe conditions, using sulfuric acid in boiling acetic acid as catalyst (5). We used the same catalyst for the cyclization of compounds (III) and obtained 5,7-dinitrobenzofurans in 30-45% yield. The *O*-(2,4-dinitrophenyl) oximes of acetone, acetophenone and cyclohexanone were cyclized to 5,7-dinitro-2-methylbenzofuran, 5,7-dinitro-2-phenylbenzofuran and 6,8-dinitro-1,2,3,4-tetrahydrodibenzofuran respectively.

EXPERIMENTAL

t-Butyl *N*-(2,4-Dinitrophenoxy)carbamate (I).

2,4-Dinitrochlorobenzene (20.2 g., 0.1 mole) in ethanol (200 ml.) was added dropwise to a stirred solution of *t*-butyl *N*-hydroxycarbamate (4) (13.3 g., 0.1 mole) and potassium hydroxide (5.6 g., 0.1 mole) in ethanol (200 ml.). The solution which turned deep



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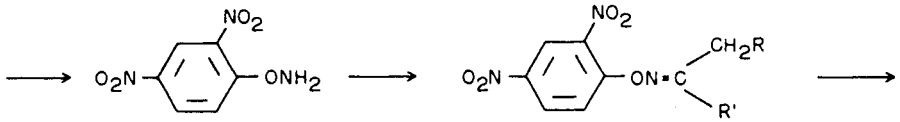
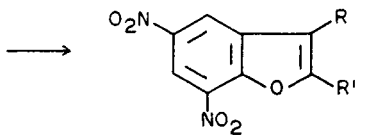


II III



IV

red was stirred for an additional hour and then glacial acetic acid was added dropwise until the color of the solution changed to light yellow. It was poured into cold water (1.5 l.). The yellow oil which separated solidified after a few minutes and was filtered, dried and crystallized from ethyl acetate-hexane. The yield was 16.4 g. (53%) of light yellow plates, m.p. 74-75°.

Anal. Calcd. for $C_{11}H_{13}N_3O_7$: C, 44.15; H, 4.38; N, 14.04. Found: C, 44.42; H, 4.40; N, 14.15.

O-(2,4-Dinitrophenyl)hydroxylamine (II).

t-Butyl *N*-(2,4-dinitrophenoxy)carbamate (I) (4 g.) was dissolved in trifluoroacetic acid (15 ml.). A strong evolution of carbon dioxide occurred. After 10 minutes at room temperature the solution was poured into ice water (100 ml.). A yellow oil separated and immediately solidified. Crystallization from ethanol yielded 2.5 g. (95%) of II as orange prisms m.p. 112° λ max (EtOH), 295 mμ (ϵ = 11,000).

Anal. Calcd. for $C_6H_5N_3O_5$: C, 36.19; H, 2.53; N, 21.10. Found: C, 36.14; H, 2.97; N, 21.50.

The infrared spectrum (nujol) showed the two $-NH_2$ bands at 3.1 and 3.15 μ.

O-(2,4-Dinitrophenyl)oximes (III).

A. From Crystalline II.

A solution of *O*-(2,4-dinitrophenyl)hydroxylamine (2 g., 0.01 mole) and the carbonyl compound (0.01 mole) in ethanol (50 ml.) was heated to boiling. A few drops of concentrated hydrochloric acid were added and the solution left at room temperature. Precipitation occurred usually within 5 minutes, but in some cases cooling in an ice bath was necessary. After filtration the products were crystallized from ethanol.

B. From I.

The *t*-butyloxycarbonyl derivative (I) (0.3 g.) was treated with trifluoroacetic acid (1 ml.) as described above and the solution added to the carbonyl compound (0.2 g.) in ethanol (3 ml.). The dinitrophenyloximes (III) precipitated out immediately or after a short cooling.

Acetone *O*-(2,4-Dinitrophenyl)oxime.

Yield, 85% (Procedure A), m.p. 87°.

Anal. Calcd. for $C_9H_9N_3O_5$: C, 45.19; H, 3.79; N, 17.57. Found: C, 45.25; H, 3.82; N, 17.20.

Acetophenone *O*-(2,4-Dinitrophenyl)oxime.

Yield, 87% (Procedure A), m.p. 175°.

Anal. Calcd. for $C_{14}H_{11}N_3O_5$: C, 55.82; H, 3.68; N, 13.95. Found: C, 55.67; H, 3.95; N, 13.80.

Cyclohexanone *O*-(2,4-Dinitrophenyl)oxime.

Yield, 78% (Procedure A), m.p. 85°.

Anal. Calcd. for $C_{12}H_{13}N_3O_5$: C, 51.61; H, 4.69; N, 15.05. Found: C, 51.99; H, 5.02; N, 14.85.

5,7-Dinitrobenzofurans (IV).

To compounds of the type (III) (0.02 mole) in acetic acid (36 ml.) sulfuric acid (12 ml.) was added. The solution was refluxed for 3 hours, cooled and poured into ice water (200 ml.). The dark precipitate was filtered and crystallized twice (charcoal) from acetic acid.

The compounds prepared are:

5,7-Dinitro-2-methylbenzofuran.

Yield, 44%, yellow needles, m.p. 162-163° (lit. (6) m.p. 165°) λ max (EtOH), 223 mμ (ϵ = 19,000), 269 mμ (ϵ = 12,800).

Anal. Calcd. for $C_9H_6N_2O_5$: N, 12.61. Found: N, 12.48.

5,7-Dinitro-2-phenylbenzofuran.

Yield, 35%, orange-yellow cubes, m.p. 231-233°; λ max (EtOH), 279 mμ (ϵ = 27,000), 357 mμ (ϵ = 10,400).

Anal. Calcd. for $C_{14}H_8N_2O_5$: C, 59.16; H, 2.84; N, 9.86. Found: C, 58.94; H, 2.87; N, 9.90.

6,8-Dinitro-1,2,3,4-tetrahydrodibenzofuran.

Yield, 31%, yellow needles, m.p. 185-186°; λ max (EtOH), 229 mμ (ϵ = 20,400), 273 mμ (ϵ = 13,000).

Anal. Calcd. for $C_{12}H_{10}N_2O_5$: C, 54.97; H, 3.84; N, 10.68. Found: C, 54.85; H, 4.04; N, 10.81.

REFERENCES

(1) T. Sheradsky, *Tetrahedron Letters*, 5225 (1966).

(2) O. L. Brady and C. D. Thomas, *J. Chem. Soc.*, **121**, 2106 (1922); O. L. Brady and R. Truszkowski, *ibid.*, **125**, 1087 (1924).

(3) A. O. Ilvespaa and A. Marxer, *Helv. Chim. Acta*, **46**, 2009 (1963).

(4) A. L. Carpino, C. A. Giza and B. A. Carpino, *J. Am. Chem. Soc.*, **81**, 955 (1959).

(5) D. S. Deorha and S. S. Joshi, *J. Org. Chem.*, **26**, 3527 (1961).

(6) W. J. Hale, *Ber.*, **45**, 1601 (1912).

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